Sludge, treated biowaste and soil — Determination of mercury in aqua regia and nitric acid digests — Cold vapour atomic absorption spectrometry or cold vapour atomic fluorescence spectrometry

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Contents

Foreword

This document Bt/TF151 WI CSS 99030 has been prepared by CEN/BT/Task Force 151 – Horizontal Standards in the Field of Sludge, Biowaste and Soil, the secretariat of which is held by Danish Standards.

This document has been prepared under a mandate given to CEN by the European Commission and the European Free Trade Association, and supports essential requirements of EU Directive(s).

For relationship with EU Directive(s), see informative Annex A, B, C or D, which is an integral part of this document.

This standard is applicable and validated for several types of matrices. The table below indicates which ones.

[table to be filled and amended by the standards writer]

Material	Validated for (type of sample, e.g. municipal sludge, compost)	Document
Sludge	2 sludges	(reference)
Soil	2 soils	
Soil improvers	Not validated yet	
Treated biowaste	Compost	
Waste		

Introduction

This document is developed in the project 'Horizontal'. It is the result of a desk study "Horizontal no 20 AAS" and aims at evaluation of the latest developments in assessing mercury in sludge, soil, treated biowaste and neighbouring fields. After an evaluation study, in which e.g. the ruggedness of the method was studies, a European wide validation of the draft standard has taken place. The results of the desk studies as well as the evaluation and validation studies have been subject to discussions with all parties concerned in CEN. The standard is part of a modular horizontal approach in which the standard belongs to the analytical step.

Until now test methods determining properties of materials were often prepared in Technical Committees (TCs) working on specific products or specific sectors. In those test methods often steps as sampling, extraction, release or other processing, analyses, etc were included. In this approach it was necessary to develop, edit and validate similar procedural steps over and over again for every material or product. Consequently this has resulted in duplication of work. To avoid such duplication of work for parts of a testing procedure references to parts of test methods from other TCs were introduced. However the following problems are often encountered while using references in this way: 1) The referenced parts are often not edited in a way that they could easily be referred to, 2) the referenced parts are often not validated for the other type of material and 3) the updates of such test standards on products might lead to inadequate references.

In the growing amount of product and sector oriented test methods it was recognised that many steps in test procedures are or could be used in test procedures for many products, materials and sectors. It was supposed that, by careful determination of these steps and selection of specific questions within these steps, elements of the test procedure could be described in a way that can be used for all materials and products or for all materials and products with certain specifications.

Based on this hypothesis a horizontal modular approach is being investigated and developed in the project 'Horizontal'. 'Horizontal' means that the methods can be used for a wide range of materials and products with certain properties. 'Modular' means that a test standard developed in this approach concerns a specific step in assessing a property and not the whole ” chain of measurement” (from sampling to analyses). A beneficial feature of this approach is that “modules” can be replaced by better ones without jeopardizing the standard “chain”.

The use of modular horizontal standards implies the drawing of test schemes as well. Before executing a test on a certain material or product to determine certain characteristics it is necessary to draw up a protocol in which the adequate modules are selected and together form the basis for the test procedure.

The modules that relates to this standard are specified in section XX Normative references.

An overview of modules and the manner, in which modules are selected will be worked out later, at which time proper reference in this standard will be provided.

The texts of the chapters 1 to 12 are normative; annexes are normative or informative, as stated in the top lines of the annexes.

1   Scope

This European Standard specifies a method for the determination of mercury in nitric acid digest or aqua regia extract of soil, sludge and treated biowaste, obtained in accordance with ISO 11466 using cold-vapour atomic absorption spectrometry. Alternatively a cold vapour atomic fluorescence spectrometric method may be used.

The matrix of the solution analyzed is dominated by the acids used in the digestion step. Tin(II)-chloride as a reduction substance is recommended in this standard, because sodium borohydride reduces many elements commonly found in soil, sludge and waste extract solutions, to the elemental state, which may cause matrix problems under particular circumstances. However, it is still possible to use sodium borohydride as reduction agent. The concentration range 0,1 µg/l – 10 µg/l in the digested solution, corresponding to 0,005 µg/l – 0,5 µg/g of mercury when a 2,0 g sample has been digested, can be determined directly. Higher concentrations can be determined if the digested solution is diluted.

2   Normative references

The following referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

EN ISO 3696:1997, *Water for analytical laboratory use — Specification and test methods.*

ISO 5725-1:1994, *Accuracy (trueness and precision) of measurement methods and results — Part 1: general principles and definitions.*

CSS99031 *Sludge, treated biowaste, and soils in the landscape – Sampling – Framework for the preparation and application of a sampling plan*

CSS99058 *Sludge, treated biowaste, and soils in the landscape – Sampling – Part 1: Guidance on selection and application of criteria for sampling under various conditions*

CSS99057 Sludge, treated biowaste, and soils in the landscape – Sampling – Part 2: Guidance on sampling techniques

CSS99032 Sludge, treated biowaste, and soils in the landscape – Sampling - Part 3: Guidance on sub-sampling in the field

CSS99059 Sludge, treated biowaste, and soils in the landscape – Sampling – Part 4: Guidance on procedures for sample packaging, storage, preservation, transport and delivery

CSS99060 Sludge, treated biowaste, and soils in the landscape – Sampling – Part 5: Guidance on the process of defining the sampling plan

CSS99034 Soil, sludge and treated biowaste – Guidance for sample pre-treatment

CSS99025A Soil, sludge and treated biowaste – Microwave digestion for the extraction of nitric acid soluble fraction of trace elements

CSS99025B Soil, sludge and treated biowaste – Digestion for the extraction of aqua regia soluble fraction of trace elements

ISO 16772: 2004, *Soil quality — Determination of mercury in aqua regia soil extracts with cold-vapour atomic absorption spectrometry or cold-vapour atomic fluorescence spectrometry.*

ISO 11466, *Soil quality — Extraction of trace elements soluble in aqua regia.*

3   Principle

Mono- and divalent mercury is reduced to the elemental form by tin(II)-chloride solution or sodium borohydride in acid medium. Elemental mercury is stripped off from the solution in a closed system, by means of a stream of nitrogen or mercury-free air. The mercury vapour, in the form of an atomic gas, passes through a cell positioned in the light path of an atomic absorption spectrometer. Its absorbance at a wavelength of 253,7 nm is measured. The absorbance signal is a function of mercury concentration, and the concentrations are calculated using a calibration curve.

Alternatively, after the reduction step, the mercury vapour is injected into the cell of an atomic fluorescence spectrometer where the mercury atoms are excited by radiation of a specific wavelength, usually about 254 nm. The intensity of the fluorescence radiation is a function of mercury concentration, and are linear over 10^6 to 10^7 orders of concentration.

4   Interferences and sources of errors

As the samples are digested before determination of mercury, there is no problem with organic substances that can absorb in the UV range. Neither are there any problems with mercury compounds which cannot be fully reduced with tin(II) chloride alone. The interference due to the presence of other elements in the matrix are dependent on their concentrations. Element concentrations in excess of those listed in Table 1 may cause negative bias. Iodide in concentrations > 0,1 mg/l causes interferences in the determination due to the formation of mercury complexes. In this case the other reduction agent, sodium tetrahydroborate, may be used.

The presence of water vapour or aerosol in the fluorescence cell may cause suppression due to quenching. Water vapour should be removed from the carrier gas stream using a hygroscopic membrane before entering the detector. The noble metals, such as gold and silver, amalgamate with mercury and, therefore, may cause suppression. Also anions, for instance sulphide, iodide and bromide, which complex strongly with mercury, can cause suppression.

Less interferences arises from heavy metals when tin(II) chloride is used rather than sodium tetrahydroborate. When flow systems are used, interference effects due to heavy metals may be less than indicated in Table 1.

Table 1 —Acceptable concentrations of some matrix elements in a measurement solution, in mg per l

Element	Atomic absobsorbance
Cu(II)	500
Ni(II)	500
Ag(I)	1
I⁻	0,1
As(V)	0,5
Bi(III)	0,5
Sb(III)	0,5
Se(IV)	0,05

5   Reagents

All reagents shall be of recognised analytical grade with particularly low mercury content. Use deionized water or water distilled from an all-glass apparatus, complying with grade 2 as defined in ISO 3696. The water used for blank determinations, and for preparing reagents and standard solutions shall have a mercury concentration that is negligible compared with the lowest concentration to be determined in the sample solutions.

5.1   Argon or nitrogen, with a purity of $\geq$ 99,99 %.

NOTE   For atomic fluorescence measurements argon should always be used, as nitrogen results in a significant signal reduction due to quenching of excited mercury atoms.

7.1   Hydrochloric acid, 37 %; ρ ~ 1,18 g/ml

The same batch of hydrochloric acid shall be used throughout the procedure.

7.2 Nitric acid, 65 %; ρ ~ 1,40 g/ml

The same batch of nitric acid shall be used throughout the procedure.

7.2.1 Nitric acid, diluted solution

Pour 250 ml of water into a 500 ml volumetric flask. Add 50 ml of nitric acid (7.2) with caution, mix and fill to the mark with water. The acid concentration is corresponding to the digested sample when it has been diluted to a 100 ml solution.

7.2.2 Nitric acid, rinsing solution for glassware, ~ 2 mol/l

Add 150 ml of nitric acid (7.2) to about 500 ml of water, and dilute with water to 1000 ml.

7.3   Aqua regia, diluted solution (1 + 9)

Add 21 ml hydrochloric acid (7.1) and 7,5 ml nitric acid (7.2) to 500 ml of water in a 1000 ml volumetric flask, mix and fill to the mark with water.

7.4   Tin(II)-chloride solution, 10 % (m/v)

Dissolve 10 g of SnCl2.2H2O in 30 ml of hydrochloric acid (7.1), transfer to a 100 ml volumetric flask and fill to the mark with water. The blank concentration of mercury can be reduced by bubbling a stream of nitrogen through the solution for 30 minutes, if necessary. Prepare this solution on the day of use.

A solution of lower concentration, e.g. 0,5 g in 100 ml, may be used with flow systems. Prepare this latter solution freshly the day of use from the more concentrated solution by diluting with water.

7.5   Sodium borohydride solution, 30 g/l

1 g sodium hydroxide, NaOH, is weighed into a 100 ml volumetric flask and dissolved in water. 3 g sodium borohydride, NaBH4, is weighed and dissolved in the sodium hydroxide solution, then diluted to the mark with water.

7.6   Mercury stock solution, 1 000 mg/l

Use a commercially available quantitative stock solution with a mercury concentration of (1000 ± 2) mg/l. This solution is considered to be stable for at least one year, but in reference to guaranteed stability, see the recommendations of the manufacturer.

7.7   Mercury, standard solution I, 100 mg/l

Pipette 10 ml of the stock mercury solution (7.6) into a 100 ml volumetric flask, add 10 ml nitric acid (7.2), mix and fill to the mark with water.

7.8   Mercury, standard solution II, 1 mg/l

Pipette 1 ml of the standard mercury solution I (7.7) into a 100 ml volumetric flask, add 10 ml nitric acid (7.2), mix and fill to the mark with water.

7.9   Mercury, standard solution III, 100 µg/l

Pipette 10 ml of the standard mercury solution II (7.8) into a 100 ml volumetric flask, add 10 ml nitric acid (7.2), mix and fill to the mark with water.

6   Apparatus

All glassware shall be carefully cleaned for low trace element determinations, e.g. by immersion in nitric acid rinsing solution solution (7.2.2) for a minimum of 6 h, followed by rinsing with water before use. The nitric acid shall be replaced each week.

8.2 Atomic absorption spectrometer (AAS)

Instrument equipped with an appropriate monitoring system, with a cold vapour generation systemand a quartz or glass tube atomizer. As readiation source use an hollow cathode lamp or, preferably, an electrodeless discharge lamp (which give a greater and more stable light intensity) operated at a current recommended by the lamp and instrument manufacturer. An AAS system with background correction device is recommended.

8.3 Atomic fluorescence spectrometer (AAS)

It is equipped with a specific Hg lamp, a fixed 254 nm filter, a photomultiplier tube for the detection of fluorescence radiation and a suitable software for processing the output signal. Operate at a current recommended by the lamp or the instrument manufacturer. The argon gas supply should be with a two stage regulator. The use of a gas purifier consisting of activated carbon is recommended. Nitrogen gas will have reduced sensitivity.

8.4   Automated sample introduction system

Automated mercury flow systems (flow injection systems or continuous flow systems) are very common both for cold vapour atomic absorption spectrometry and atomic fluorescence spectrometry. They allow a concentration range lower by about one order of magnitude. Manually operated systems or semi-automated batch systems are adequate as well.

8.5 Cold-vapour generator, batch system or an automated flow injection analysis system (FIAS)

The system should be adaptable to the atomic absorption spectrometer (8.2) or to the atomic fluorescence spectrometer (8.3), according to the detection technique used for the determination of mercury. A flow-controlled nitrogen (7) or argon stream (7) is used as an inert carrier to transport mercury vapour into the cell. Time-controlled addition of tin(II)-chloride reducing solution (7.4) in combination with automatic start of the read signal of the spectrometer is required. Systems with a 10 cm quartz cell with quartz windows adapted for atomic absorption spectrometry (8.2) are commercially available. In this case, the quartz cell is electrically heated to a temperature of 60 - 100 °C to avoid condensation of water. For the atomic fluorescence spectrometer (8.3), condensation in the cell is avoided by the inclusion of a drying tube in the detection system.

NOTE   If an automated system is used, where the reaction occurred continuously (FIA-System), the concentration of stannous chloride solution, reaction time and the gas-liquid separator configuration must be optimised due to the slow reaction kinetics of the reducing system.

Warning - It is essential that the manufacturer's safety recommendations are strictly observed.

7   Sampling and sample pre-treatment

7.1   Sampling

Sampling shall be carried out in accordance with sampling standards CSS99031-32 and 99057-60.

Samples shall be stored in suitable containers with an appropriate closure material such as PTFE. Samples to be frozen may be stored in glass containers pre-cleaned by rinsing in nitric acid (7.2.2) for one night.

Samples shall be kept cold (< 8°C) and in the dark. The sample pre-treatment shall take place within 24 h of sampling. Alternatively, freeze the samples (-18 °C) directly after sampling and keep frozen for a maximum of one month before sample pre-treatment.

Transfer a sub-sample, homogenized according to CSS99034 (Horizontal standard module(s) for pre-treatment of solid materials) of approximately 100 g to a porcelain dish.

Store the ground material in a desiccators or a tightly closed glass container.

7.2   Sample pre-treatment

Transfer a sub-sample, homogenized according to CSS99034 (Horizontal standard module(s) for pre-treatment of solid materials) of approximately 100 g to a porcelain dish.

Store the ground material in a desiccators or a tightly closed glass container.

8   Procedure

8.1   Test solution

The nitric acid or aqua regia digested samples (CSS99025 A or B) are transferred to 100 ml volumetric flasks and filled to the mark with water. The digested samples are prepared according to the Horizontal standards for digestion of soil, sludge and waste with nitric acid or aqua regia, respectively. The aqua regia samples should be diluted 1 + 9 with water before the determination of mercury.

8.2   Blank test solution

Carry out a blank test at the same time as the extraction with nitric acid or aqua regia following the sample procedure, using the same quantities of all reagents for the determination, but omitting the test sample. Transfer 10 ml of the blank test solution to a 100 ml volumetric flask and fill to the mark with water.

8.3   Preparation of the calibration solutions

Before each batch of determinations, prepare a blank calibration solution and from the 100 μg/l mercury standard solution III (7.8) at least five calibration solutions covering the range of concentrations to be determined.

Pipette 1 ml, 2 ml, 5 ml, 10 ml and 20 ml of mercury standard solution (7.8) into a series of 100 ml volumetric flasks. Fill to the mark with diluted nitric acid solution (7.2.1) or diluted aqua regia solution (7.3) and mix well. These solutions correspond to mercury concentrations of 1 μg/l, 2 μg/l, 5 μg/l, 10 μg/l and 20 μg/l, respectively. Using 10 ml of each solution for the cold-vapour generator these solutions correspond to 10 ng, 20 ng, 50 ng, 100 ng and 200 ng of mercury, respectively.

8.4   Calibration

8.4.1   Cold vapour atomic absorption spectrometer (CV-AAS)

Set up the atomic absorption spectrometer (8.2) and the cold-vapour generator (8.4) according to the manufacturer's instructions, select a wavelength of 253,7 nm and adjust the quartz cell, the gas flow and the reaction time and flow rate of tin(II)-chloride solution (7.4) or sodium borohydride solution (7.5) to get maximum transmission intensity. Transfer 10 ml of blank calibration solution (10.3) into the cold-vapour generation bottle, connect the bottle to the system and start the time-controlled programme. The signal of the blank calibration solution should be negligible compared to with the lowest standard solution.

8.4.2   Cold vapour atomic fluorescence spectrometer (CV-AFS)

Set up the atomic fluorescence spectrometer (8.3) and the cold-vapour generator (8.4) according to the manufacturer's instructions. Adjust the quartz cell (if the instrument is equipped with one), the gas flow and the flow rate of stannous chloride or sodium borohydride. Wait until the system is in equilibrium. Aspirate a blank and start the measurement procedure. The signal should be negligible.

8.5   Plotting the calibration graph

Plot a graph having the mercury concentrations of the calibration solutions (10.3), from which the blank calibration solution reading has been subtracted, as abscissa, and the corresponding signal values as ordinate.

8.6   Measurement of test sample

Transfer 10 ml of blank test solution (10.2) into the cold-vapour generator bottle, connect the bottle to the system and start the time-controlled programme and record the signal. Repeat the measurement with each test solution (10.1), and record the signal.

If the mercury concentration of the test solution exceeds the range of calibration, the test solution shall be diluted with diluted nitric acid solution (7.2.1), or diluted aqua regia solution (7.3) accordingly.

NOTE   The standard addition method can be used to check the absence of matrix effects. If the analytical results according to the standard addition method and the calibration curve method are equal, the calibration curve method can be applied.

8.7   Quality Assurance of the overall procedure

8.7.1   Analysis of CRM

Analyse a test sample of a certified reference material with matrix comparable to the samples to be analysed.

8.7.2   Analysis of spiked natural samples

Analyse at least one spiked natural sample for each 20 samples in each series of samples:

Spike 50 µl or 100 µl of the metal stock solution (7.6) to an aliquot of a test sample. Establish a control limit for recovery of the spike based for example on precision data in Annex ? or on laboratory precision data.

NOTE   If the recovery is outside the control limits, the whole series of analyses should be repeated.

8.7.3   Duplicate determination

Analyse two individual test samples of each dried, homogenised sample submitted for analysis. Establish a control limit for the difference between results for the two sub-samples based for example on precision data in Annex A or on laboratory precision data.

9   Expression of results

9.1 Method of calculation

By reference to the calibration graph obtained, determine the concentration of the element corresponding to the signal of the test solution (7.1) and of the blank test solution (7.2). Calculate the mass fraction of mercury (w) in the sample, expressed as µg/g per dried matter using the equation:

$$w = (\rho - \rho_0) \times f \times V / m$$

where

w is the mass fraction of mercury in the sample, in µg/g dry matter;

ρ is the mercury concentration, corresponding to the signal of the test portion (7.1), in µg/l;

ρ_0 is the mercury concentration, corresponding to the signal of the same blank (7.2), in µg/l;

f is the dilution factor if the test solution (7.1) is diluted before the determination step;

V is the volume, of the digested solution after dilution to the mark (usually 100 ml), in l;

m is the mass of the sample, in kg.

9.2   Expression of results

The result shall be expressed in mg/kg dry matter and reported to two significant figures. Values shall be rounded to 0,01 µg/g, but only significant figures shall be expressed.

EXAMPLE w(Hg) = 0,45 µg/g dry matter

                        w(Hg) = 12,5 µg/g dry matter

10 Precision data

The performance characteristics of the method (Annex A) data have been evaluated. Table 2 gives the resulting typical values for repeatability and reproducibility limits as their observed ranges. The typical value is derived from the data in Table A.2 in Annex A by taking the median value and rounding the numbers.

Table 2 — Typical values and observed ranges of the repeatability and reproducibility limits

The reproducibility limit provides a determination of the differences (positive and negative) that can be found (with a 95 % statistical confidence) between a single test result obtained by a laboratory using its own facilities and another test result obtained by another laboratory using its own facilities, both test results being obtained under the following conditions : The tests are performed in accordance with all the requirements of the present standard and the two laboratory samples are obtained from the same primary field sample and prepared under identical procedures. Conversely, the repeatability limit refers to measurements obtained from the same laboratory, all other conditions being identical. The reproducibility limit and the repeatability limit do not cover sampling but cover all activities carried out on the laboratory sample including its preparation from the primary field sample.		
Results of the validation of Determination of mercury in aqua regia and nitric acid digests – Cold vapour atomic absorption spectrometry or cold vapour atomic fluorescence spectrometry in soil, sludge and treated biowaste	Typical value %	Observed range %
Repeatability limit, r	23	*11 - 33*
Reproducibility limit, R	63	34 - 83

NOTE 1.   The above results refer to the difference that may be found between two test results performed on two laboratory samples obtained under the same conditions. In the case when reference is made to the dispersion of the values that could reasonably be attributed to the parameter being measured, the above typical reproducibility values and observed reproducibility ranges should be divided by $\sqrt{2}$ to obtain the corresponding typical dispersion limit and its observed range. In the example of Hg in Sludge 2 the result and its dispersion limit is 0.66 ± 0.31 mg/kg (2 * sR = 47 % of 0.66). This means that with a 95 % statistical confidence, the values reasonably attributable to the measured parameter are larger than 0.35 mg/kg and lower than 0.97.

NOTE 2. The repeatability limit (r) and the reproducibility limit (R) as given in Table A.2 (Annex A) and in this table are indicative values of the attainable precision if the determination of mercury in aqua regia and nitric acid digests – Cold vapour atomic absorption spectrometry or cold vapour atomic fluorescence spectrometry is performed in accordance with this standard [CSS99030].

NOTE 3 A limited number of materials and parameters were tested. Consequently, for other materials and parameters, performance characteristics may fall outside the limits as derived from the validation of the the determination of mercury in aqua regia and nitric acid digests – Cold vapour atomic absorption spectrometry or cold vapour atomic fluorescence spectrometry in soil, sludge and treated biowaste.

NOTE 4   In particular for relatively heterogeneous materials, the repeatability and the reproducibility limits may be larger than the values given in Table A.2 (Annex A) and this table.

10 Test report

The test report shall contain the following information:

a)   a reference to this European Standard including its date of publication;

b)   precise identification of the sample;

c)   expression of results, according to 11.2;

d)   any deviation from this standard, and any facts which may have influenced the result. Where the test is not carried out in accordance with this standard, reference may only be made to EN xxxx:2003 in the report in case all deviations from the procedures prescribed in this standard are indicated in the report stating the reason for deviation.

11 Performance characteristics

An interlaboratory test has to be performed to yield precision data.

Annex A
(informative)

Repeatability and reproducibility data

A.1 Performance characteristics

A.1.1 Objective of the interlaboratory comparison

In a European wide interlaboratory comparison study according to ISO 5725-2, the performance characteristics of the standard "Determination of mercury in aqua regia and nitric acid digests – Cold vapour atomic absorption spectrometry or cold vapour atomic fluorescence spectrometry in soil, sludge and treated biowaste" were established.

A.1.2 Materials used in the interlaboratory comparison study

The interlaboratory comparison of determination of mercury in aqua regia and nitric acid digests – Cold vapour atomic absorption spectrometry or cold vapour atomic fluorescence spectrometry in soil, sludge and treated biowaste was carried out with 7 European laboratories on 5 materials. The materials selected for the interlaboratory comparison were chosen to represent soil, sludge and biowaste as broad as possible, because the standard will find general application across different types of soil and soil related materials. (detailed information can be found in the final report on the Interlaboratory comparison study mentioned in the Bibliography).

In the interlaboratory comparison study the following starting points were used:

- The laboratory samples were all taken from one large batch of the different materials according to the normal practice. The normal size reduction and the normal repeated mixing were carried out as needed to obtain representative laboratory samples from the large batch sample (ref JRC).

  - Note : the samples provided for the validation should not be confused with reference samples provided for certification purposes, as the performance results obtained have to be directly applicable to daily practice (less rigorous sample preparation than for a reference material).

- The experimental plan was designed by project HORIZONTAL on the basis of each laboratory being given two laboratory samples of each material to be tested. This is in accordance with ISO 5725-2.

- The materials examined cover all the grain size classes to which the the determination of mercury in aqua regia and nitric acid digests – Cold vapour atomic absorption spectrometry or cold vapour atomic fluorescence spectrometry in soil, sludge and treated biowaste applies: very fine grained materials (like sludge: 0 µm to about 125 µm) and fine-grained materials (soil and compost: 0 mm to 4 mm).

Table A.1 provides a list of the types of materials chosen for testing and the selected components.

Table A.1 — Material types tested and components analysed in the interlaboratory comparison of the Determination of mercury in aqua regia and nitric acid digests – Cold vapour atomic absorption spectrometry or cold vapour atomic fluorescence spectrometry in soil, sludge and treated biowaste.

Grain size class	Sample code	Material type tested	Parameters/congeners
Sludge (<0.5 mm)	Sludge 1	Mix 1 of municipal WWTP sludges from North Rhine Westphalia, Germany	Hg
	Sludge 2	Mix 2 of municipal WWTP sludges from North Rhine Westphalia, Germany	Hg
Fine grained (< 2 mm)	Compost 1	Fresh compost from Vienna, Austria	Hg
	Compost 2	Compost from Germany	
	Soil 1	A sludge amended soil from Pavia	Hg
	Soil 2	A sludge amended soul from Düsseldorf	Hg

A.1.3 Interlaboratory comparison results

The statistical evaluation was conducted according to ISO 5725-2. The average values, the repeatability standard deviation (s_r) and the reproducibility standard deviation (s_R) were obtained (Table A.2).

The repeatability is determined as an interval around a measurement result (i.e. "repeatability limit"). This interval corresponds to the maximum difference that can be expected (with a 95% statistical confidence) between one test result and another, both test results being obtained under the following conditions: The tests are performed in accordance with all the requirements of the present standard by the same laboratory using its own facilities and testing laboratory samples obtained from the same primary field sample and prepared under identical procedures.

The repeatability limit was calculated using the relationship : $r_{test} = f \cdot \sqrt{2} \cdot s_{r,test}$ with the critical range factor f = 2.

For instance, the repeatability limit around a measurement result of 0.5 mg Hg /kg is ± 0.1 mg Hg /kg (i.e ± 23 % of 0.5).

NOTE The above relationship refers to the difference that may be found between two measurement results performed each on two laboratory samples obtained under the same conditions. The value f = 2 used in the factor f · $\sqrt{2}$ corresponds to the theoretical factor of 1,96 for a pure normal distribution at 95 % statistical confidence. Also, this value f = 2 corresponds to the usual value k = 2 of the coverage factor recommended in the Guide to the expression of Uncertainty in Measurement (GUM). However it may be necessary to use a larger value for f in situation as described in clause 12.

The reproducibility, like repeatability is also determined as an interval around a measurement result (i.e. "reproducibility limit"). This interval corresponds to the maximum difference that can be expected (with a 95% statistical confidence) between one test result and another test result obtained by another laboratory, both test results being obtained under the following conditions : The tests are performed in accordance with all the requirements of the present standard by two different laboratories using their own facilities and testing laboratory samples obtained from the same primary field sample and prepared under identical procedures.

The reproducibility limit was calculated using the relationship: $R = f \cdot \sqrt{2} \cdot s_R$ with the critical range factor f = 2.

For instance, the reproducibility limit around a measurement result 0.5 mg Hg /kg is ± 0.3 mg Hg /kg (i.e ± 63 % of 0.5).

NOTE The above relationship refers to the difference that may be found between two measurement results performed each on two laboratory samples obtained under the same conditions. The value f = 2 used in the factor f · $\sqrt{2}$ corresponds to the theoretical factor of 1,96 for a pure normal distribution at 95 % statistical confidence. Also, this value f = 2 corresponds to the usual value k = 2 of the coverage factor recommended in the Guide to the expression of Uncertainty in Measurement (GUM). In the case when reference is made to the dispersion of the values that could reasonably be attributed to the parameter being measured, the dispersion limit is equal to k · s_R with the usual value k = 2, resulting in a dispersion limit lower than the reproducibility limit (i.e. a ratio of $\sqrt{2}$). However it may be necessary to use a larger value f · $\sqrt{2}$ (or k) in situation as described in clause 12 .

In case of relatively heterogeneous materials, the repeatability and the reproducibility limits may be larger than the values given in Tables A.2 (this means that the value chosen for the critical range factor f is larger than 2 as well as for the coverage factor k for dispersion). This is because the extreme results may have been obtained in accordance with the present standard and/or be caused by the variability within, or in between, the laboratory samples.

Table A.2 — Results of the interlaboratory comparison studies of the Determination of mercury in aqua regia and nitric acid digests – Cold vapour atomic absorption spectrometry or cold vapour atomic fluorescence spectrometry. All concentrations in mg/kg.

Matrix	Parameter	Mean mg/kg	sr	sR	r	R	p	Outliers	Used number of data	Number of data reported below detection	Total no of data
Sludge 1	CV AAS Hg	1.120	4.61%	22.6%	0.145	0.708	5	2	27	0	35
Sludge 2	CV AAS Hg	0.660	8.05%	23.6%	0.149	0.436	8	0	41	0	41
Compost 2	CV AAS Hg	0.118	3.88%	12.0%	0.013	0.040	6	1	32	0	36
Soil 1	CV AAS Hg	0.070	11.8%	29.8%	0.023	0.058	7	0	38	0	38
Soil 2	CV AAS Hg	0.052	8.71%	14.7%	0.013	0.022	7	0	38	5	43

Abbreviations: sr Repeatability standard deviation; SR Reproducibility standard deviation; r Repeatability limit

(comparing two measurements); R Reproducibility limit (comparing two measurements); p Number of labs.

Bibliography